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(71) Applicant *(for all designated States except US)*: UPM-KYMMENE OY [FI/FI]; P.O. Box 40, FIN-37601 Valkeakoski (FI).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: KARHUKETO, Hannu [FI/FI]; Asevelitie 11, FIN-37601 Valkeakoski (FI).

(74) Common Representative: UPM-KYMMENE OY; Gustafsson, Helmer, P.O. Box 40, FIN-37600 Valkeakoski (FI).

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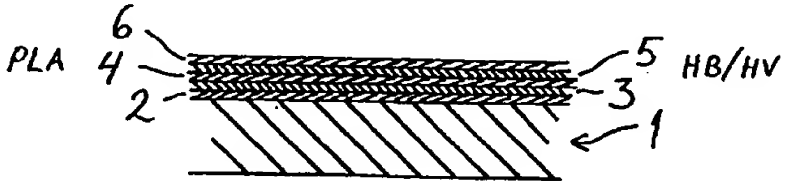

(57) Abstract

The layer material comprises a cellulose-based naturally decomposing basic layer (1) and on top of it layers (3, 5) of polyhydroxyalcanoate, such as hydroxybutyric/hydroxyvaleric copolymer (HB/HV). To produce good adhesion, surface and barrier properties to the product used as a packaging material, there is a layer (4, 2) of biodegradable polylactide (PLA) between the aforesaid layers (3, 5) and between these layers and the basic layer (1).

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LAYER MATERIAL

The invention relates to a layer material according to the introductory part of the accompanying claim 1.

It is known to make packaging laminates by combining a cellulose-based, naturally decomposing basic layer with layers of biodegradable plastic which improve the tightness of the basic layer. This way total compostability of the material in the waste management of the packaging material can be achieved.

From the European application publication 534471, for example, a biodegradable laminate used as packaging material is known. This laminate consists of polyhydroxybutyrate-based copolymer, more precisely hydroxybutyric-hydroxyvaleric copolyester (HB/HV) coextruded together with a polyethylene film on a cellulose-based sheet. The polyethylene film is used as an auxiliary film in the coextrusion process, and after the process it is pulled of the laminate leaving the hydroxybutyric/hydroxyvaleric film attached to the sheet.

The biodegradable polymer in question has good barrier properties (barrier layer properties) in itself and is therefore a popular laminating agent, and it can be used to increase the tightness of cellulose-based basic materials noticeably.

In addition, the European application publication 603876 introduces the use of hydroxybutyric/hydroxyvaleric copolymer layers as water vapour barrier on both sides of an oxygen barrier layer of polyvinyl alcohol. The layers are laminated either on one side or both with a layer of cellulosic derivative or paper.

The multi layer structure in question does not provide satisfactory properties. Polyvinyl alcohol tends to dissolve in water which makes it difficult to be used

under conditions of considerable humidity. Furthermore, the coextrusion of these materials is in practise difficult. And finally, polyvinyl alcohol is poorly compostible, in other words it is not biodegradable in the strict sense of the word.

The purpose of this invention is to provide a layer material which exhibits improvements to the aforementioned properties and which can be used as airtight and biodegradable packaging materials. To achieve this purpose, the layer material is primarily characterized in what is presented in the characteristic part of the accompanying claim 1.

The invention combines the excellent properties of polyhydroxyalcanoate and polylactide.

By using two separate polyhydroxyalcanoate layers, such as polyhydroxybutyric-based layers, particularly hydroxybutyric-hydroxyvaleric copolymer layers, good barrier properties can be achieved with layers of great thinness, even of only micrometers thick, when they are combined with polylactic acid, i.e. polylactide (PLA) which improves the processability of the material. Polylactide exhibits good adhesion properties and it does not stick to the surface of the chill roll in coextrusion which means that also the coextrusion chances of the hydroxybutyric/ hydroxyvaleric copolymers are improved, among other things edge weaving is reduced and the nucleant can be omitted.

The use of two separate polyhydroxyalcanoate layers ensures that the microscopic pinholes which may develop to the layers are not formed at the same spot, which improves barrier properties.

Because of the plastic layer structure described, the gas and grease tightness are improved, and better resistance to folding and creasing can be achieved.

The invention is described in more detail in the following with reference to the accompanying drawings in which

Figure 1 shows a schematic view of the layer material according to the invention, and

Figure 2 shows the process for manufacturing the material.

Figure 1 includes a cellulose-based and naturally decomposing basic layer 1, which gives the product its strength, the basis weight of which may vary within the known values for paper and cardboard. Laminated on top of the basic layer 1 by coextrusion, are the following layers starting from the basic layer 1: A polylactide layer 1 (PLA) which attaches the other plastic layers to the basic layer by adhesion, a hydroxybutyric/hydroxyvaleric copolymer layer 3 (HB/HV), a polylactide layer 4, a hydroxybutyric/hydroxyvaleric copolymer layer 5 and a polylactide layer 6 which forms the outer layer. As is apparent from the aforesaid, all the plastic layers are biodegradable which in this case denotes that their polymer structures are naturally such that the polymer chains degrade under compost conditions. The layer material can be used as a packaging material for purposes when the escape of water vapour, oxygen or aroma is wished to be prevented, particularly for the packaging of food stuffs, cosmetics and industrial chemicals.

The polylactide layer 4 in the middle also attaches the HB/HV layers 3 and 5, which act as barrier layers, to each other.

The HB/HV layers 3 and 5 can be formed very thin, and their barrier properties as separate layers are better than those of a uniform layer of the same total thickness.

Due to the aforesaid properties, the HB/HV qualities may be more freely selected.

The heat-sealing properties of the outermost PLA layer may be utilized in forming food stuff packaging containers or in attaching additional layers to the material. A further good property of polylactide is its inexpensiveness.

By using polylactide (PLA) and HB/HV copolymer together as several separate layers (3 layers of PLA and 2 layer of HB/HV), the good adhesion and surface properties of the first and the good barrier properties of the latter can be utilized efficiently. The plastic layers are usually in contact with the packaged product. It is also possible to further add the same layers to the layer material in Fig. 1 so that they succeed one another by turns as described. On the other hand, the outermost PLA layer 6 can be omitted, in which case the layer 5 forms the outer layer. This is suitable for liquid packaging containers because of the good water resistance of HB/HV or its equivalent. If the outer layer is PLA it is suitable to the packaging of greasy food stuffs.

In layers 3 and 5, other polyhydroxyalcanoate may also be used, preferably polyhydroxybutyrate (PHB) or its copolymer with another hydroxyalcanoate, such as the aforementioned HB/HV.

The hydroxybutyric/hydroxyvaleric copolymer may be, for example, one with 92 % of hydroxybutyric units and 8 % of hydroxyvaleric units, which is sold under the trade name "BIOPOL" by the Zeneca Ltd. The number of hydroxyvaleric units in the copolymer may vary, and it may be within, for example, the range 1 - 20 p-%.

In principle it would be possible to replace the layers 3 and 5 with only one polyhydroxyalcanoate layer mentioned above, in which case the structure in Fig.

1 would be a three-layer structure.

The basic layer 1 may be paper used in food stuff packaging containers, cardboard or preferably greaseproof paper which has good grease and aroma tightness, for example 100 - 600 s as Linden tightness. The basis weight of the basic layer may vary considerably, for example in the range 30 - 500 g/m^2.

Figure 2 shows the principle for manufacturing the layer material. The coextruder 7 comprises a feed block 8 into which the aforesaid two biodegradable polymer materials are fed (marked with letters HB/HV and PLA). The feed block arranges the materials into five layers one on top of each other, after which the forming die 9 spreads them into a film of full-width which is lead into the nip between the press roll 10 and the control roll 11, into which nip the material forming the basic layer 1 is brought from its own roll. The finished layer material is lead along the surface of the control roll 11 to further processing. In the drawing, a possibility to add an additional layer on top of the plastic layer comprised of layers 2 - 6 is marked with a dotted line, the additional layer being preferably also a cellulose-based naturally decomposing material. In this case, there could be a thinner paper on one side of the plastic layers and a thicker packaging cardboard on the other side.

Claims

1. A layer material which comprises a cellulose-based and naturally decomposing basic layer (1) and, on top of this basic layer, layers (3, 5) of polyhydroxyalcanoate, such as hydroxybutyric/hydroxyvaleric copolymer (HB/HV), **characterized** in that between the aforesaid layers (3, 5) and between these layers and the basic layer (1) there is a layer (4, 2) of biodegradable polylactide (PLA)

2. A layer material according to claim 1, **characterized** in that on top of the outermost polyhydroxyalcanoate layer, such as the hydroxybutyric/hydroxyvaleric layer (5), there is also a layer (6) of biodegradable polylactide as the outer layer to the plastic layers.

3. A layer material according to claim 1 or 2, **characterized** in that the plastic layers (2 - 6) are formed on top of the basic layer (1) by coextrusion.

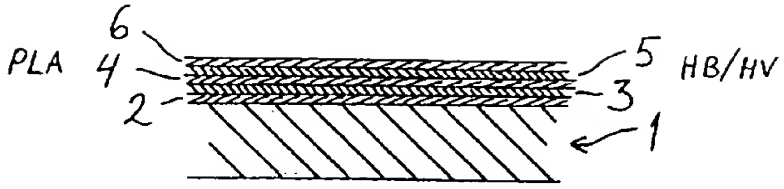

Fig. 1

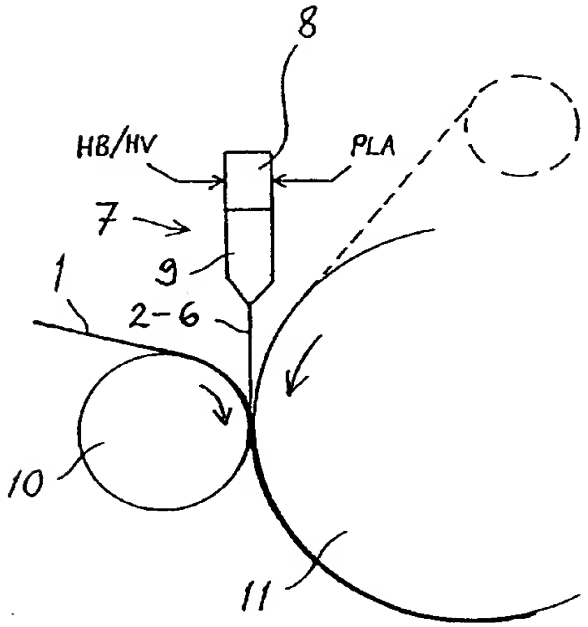

Fig. 2

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 27/10, B65D 65/46
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B32B, B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 9631303 A1 (YHTYNEET PAPERITEHTAAT OY), 10 October 1996 (10.10.96), page 6, line 1 - line 11, figure 4 --	1-3
P,Y	File WPI, Derwent accession no. 96-236165, Toyobo KK: "Biodegradable polyester adhesives having stable quality and good water resistance-contains biodegradable polyester contg. lactic acid residue and caprolactone residue", JP,A,8092359, 960409, DW9624 --	1-3
Y	WO 9406866 A1 (BIOPAK TECHNOLOGY, LTD.), 31 March 1994 (31.03.94), page 54, line 19 - page 55, line 2, claim 29 --	1-3

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
7 July 1997	21 -07- 1997
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	File WPI, Derwent accession no. 94-114861, Toppan Printing Co Ltd: "Biodegradable paper container- comprises paper laminate with bio- degradable plastic layer", JP,A,6064111, 940308, DW9414	1-3
A	DE 4430415 A1 (BUNA GMBH), 14 March 1996 (14.03.96), column 1, line 64 - column 2, line 44	1-3
A	WO 9428070 A1 (ZENECA LIMITED), 8 December 1994 (08.12.94), page 9, line 6 - line 27, claims 19, 20,21,84	1-3
A	EP 0603876 A1 (BUCK WERKE GMBH & CO), 29 June 1994 (29.06.94), column 3, line 11 - line 22	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/07/97

International application No.
PCT/FI 97/00184

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9631303 A1	10/10/96	AU 5159896 A	23/10/96
		AU 5277696 A	23/10/96
		FI 951637 A	07/10/96
		WO 9631347 A	10/10/96
WO 9406856 A1	31/03/94	AU 5128993 A	12/04/94
		EP 0662103 A	12/07/95
		JP 8501584 T	20/02/96
		US 5444113 A	22/08/95
		US 5502158 A	26/03/96
DE 4430415 A1	14/03/96	NONE	
WO 9428070 A1	08/12/94	AU 6727594 A	20/12/94
		EP 0700418 A	13/03/96
		FI 955645 A	23/11/95
		JP 8510498 T	05/11/96
		NO 954748 A	23/11/95
EP 0603876 A1	29/06/94	CZ 9302870 A	12/04/95
		DE 4244000 A	30/06/94
		PL 301609 A	27/06/94
		SK 146393 A	07/09/94